Office europ ❋ des brevets

(11) **EP 0 710 521 A1**

(12) **EUROPEAN PATENT APPLICATION**

(AN)

(43) Date of publication:
08.05.1996 Bulletin 1996/19

(51) Int. Cl.^{6}: **B23K 35/26**
// C22C13/00

(21) Application number: 95302225.8

(22) Date of filing: 03.04.1995

(84) Designated Contracting States:
DE ES FR GB

(30) Priority: 02.11.1994 JP 293880/94
21.02.1995 JP 56691/95

(71) Applicant: MITSUI MINING & SMELTING CO., LTD.
Tokyo (JP)

(72) Inventors:
• **Ninomiya, Ryuji**
  Ageo-shi, Saitama-ken 362 (JP)
• **Matsunaga, Junichi**
  Ageo-shi, Saitama-ken 362 (JP)

(74) Representative: **Perry, Robert Edward**
  GILL JENNINGS & EVERY
  Broadgate House
  7 Eldon Street
  London EC2M 7LH (GB)

(54) **Lead-free solder**

(57) A lead-free solder consisting of 1 to 4 wt% of Ag, either one or both of Bi and In of their respective amounts meeting the conditions that the value of expression (1), A, is equal to or greater than 5.00 and that the value of expression (2), B, is equal to or less than 6.90, and Sn for the balance:

$$A = [\text{Ag wt\%}] + 1.23\,[\text{Bi wt\%}] + 0.52\,[\text{In wt\%}] \quad (1)$$

$$B = [\text{Ag wt\%}] + 1.19\,[\text{Bi wt\%}] + 0.50\,[\text{In wt\%}] \quad (2)$$

This solder has a tensile strength and an elongation as high as those of conventional Pb-Sn solder without containing neither lead nor cadmium which can cause environmental contamination.

EP 0 710 521 A1

Description

BACKGROUND OF THE INVENTION

5   a) Field of the Invention

This invention relates to a lead-free solder which has mechanical properties as good as those of conventional Pb-Sn solder.

10   b) Description of the Prior Art

Pb-Sn alloy of eutectic or near-eutectic composition is well known as a representative solder. Zn-Cd alloy, which has a greater strength than Pb-Sn eutectic solder, is also known. Amid the increased concern with environmental protection in recent years, the harmfulness of lead and the noxious effect of vaporized cadmium on workers have become
15   a problem with the former and latter solders, respectively, and a solder replacing them is needed.

To meet this need, zinc or tin base solders which contain neither harmful lead nor cadmium were proposed. The solders hitherto proposed, however, do not have the mechanical properties as good as conventional Pb-Sn solder. 3.5Ag-Sn solder, for example, has a problem of a low tensile strength, though it has a satisfactory elongation. In this present situation, a solder which does not contain harmful lead or cadmium and has both a satisfactory high tensile strength
20   and a satisfactory high elongation.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a solder which does not contain harmful elements such as lead and
25   cadmium and still has both a tensile strength and an elongation as high as those of Pb-Sn solder.

The solder of the present invention consists of 1 to 4 wt% of Ag, either one or both of Bi and In of their respective amounts meeting the conditions that the value of expression (1), A, is equal to or greater than 5.00 and that the value of expression (2), B, is equal to or less than 6.90, and Sn for the balance.

30

$$A = [Ag\ wt\%] + 1.23\ [Bi\ wt\%] + 0.52\ [In\ wt\%] \tag{1}$$

$$B = [Ag\ wt\%] + 1.19\ [Bi\ wt\%] + 0.50\ [In\ wt\%] \tag{2}$$

By this composition, the solder of the present invention has a tensile strength equal to or greater than 4.0 kgf/mm^2
35   and an elongation equal to or greater than 30% which are mechanical properties as good as those of conventional Pb-Sn solder.

BRIEF DESCRIPTION OF THE DRAWINGS

40   Figure 1 shows the relationship between the amounts of In and Bi to be added when the Ag content is 1 wt% (Sn for the balance).

Figure 2 shows the relationship between the amounts of In and Bi to be added when the Ag content is 2 wt% (Sn for the balance Sn).

Figure 3 shows the relationship between the amounts of In and Bi to be added when the Ag content is 3 wt% (Sn
45   for the balance).

Figure 4 shows the relationship between the amounts of In and Bi to be added when the Ag content is 4 wt% (Sn for the balance).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

50

In the present invention, silver has an effects of improving the heat resistance, lowering the fusing temperature, and increasing the strength, spreadability and brightness of the solder by a little amount contained. The silver content appropriate for this purpose is equal to or greater than 1 wt%. The upper limit of the silver content is 4 wt%, taking into account the expensiveness of silver.

55   The Bi and In contents are within the ranges such that the combination of their contents fall in the hatched area in Figures 1 to 4 for 1 wt%, 2 wt%, 3 wt% and 4 wt%, respectively, which can be defined by the conditions that the value of expression (1), A, is equal to or greater than 5.00 and that the value of expression (2), B, is equal to or less than 6.90, where expressions (1) and (2) represent the upper and lower boundary lines of the hatched area in Figure 3.

the value of expression (2), B, is greater than 6.90, on the other hand, the elongation of the solder is lower than 30%.

Since the solder of the present invention may contain either one or both of Bi and In of the amounts as described above, it may be Sn-Ag-Bi or Sn-Ag-In ternary alloy or Sn-Ag-Bi-In quarternary alloy.

When the solder is Sn-Ag-Bi ternary alloy without In, expressions (1) and (2) become as follows:

$$A = [Ag\ wt\%] + 1.23\ [Bi\ wt\%] \tag{1'}$$

$$B = [Ag\ wt\%] + 1.19\ [Bi\ wt\%] \tag{2'}$$

From these expressions and the aforementioned range of Ag, the Bi content is greater than 0.81 wt% and smaller than 6.4 w%.

If the Bi content is smaller than 0.81 wt%, the tensile strength of the solder is lower than 4.0 kgf/mm². If greater than 6.4 wt%, the elongation of the solder is lower than 30%.

When the solder is Sn-Ag-In ternary alloy without Bi, expressions (1) and (2) become as follows:

$$A = [Ag\ wt\%] + 0.52\ [In\ wt\%] \tag{1''}$$

$$B = [Ag\ wt\%] + 0.50\ [In\ wt\%] \tag{2''}$$

From these expressions and the aforementioned range of Ag, the In content is greater than 1.9 wt% and smaller than 12 wt%.

If the In content is smaller than 1.9 wt%, the tensile strength of the solder is lower than 4.0 kgf/mm². If greater than 12 wt%, the elongation of the solder is lower than 30%. However, it is preferable to set the upper limit of the In content to 4.0 wt% because In is expensive.

When the solder is Sn-Ag-Bi-In quarternary alloy, the Bi content is within the range of 0.81 to 5.0 wt% and the In content is within the range of 1.9 to 12 wt% from expressions (1) and (2) and the range of the Ag content.

Examples

Sn, Ag, Bi, In and Pb were weighed out to prepare compositions listed in Table 1, each composition being 10 kg in total. These compositions were melted at 300 °C in an electric furnace in the air using a graphite crucilbe. After all metals had melted, the molten metals were thoroughly stirred to prevent the segregation caused by the gravity and cast into solder pieces of 10 mm in thickness using a mold of 150 mm x 60 mm with the height of 150 mm in inner dimensions. Test samples were cut from the bottom part of the solder pieces according to the JIS 4 standards with a machine, and their tensile strength and elongation were measured by the test method defined by the JIS Z2241 standards. The results are shown in Table 1. The strength and the elongation of Pb-Sn eutectic solder and 3.5Ag-Sn solder are also shown in

3

Table 1

	Chemical Composition (wt%)				Tensile Strength (kgf/mm^2)	elongation (%)
	A g	B i	I n	S n		
	1	0	8	Bal.	4.1	35.9
	1	0	9	Bal.	4.3	34.2
	1	0	10	Bal.	4.5	32.6
E	1	0	11	Bal.	4.7	31.0
x	1	1	6	Bal.	4.1	35.3
a	1	1	7	Bal.	4.3	33.7
m	1	1	8	Bal.	4.5	32.0
p	1	1	9	Bal.	4.7	30.4
l	1	2	3	Bal.	4.0	36.4
e	1	2	4	Bal.	4.2	34.8
	1	2	5	Bal.	4.4	33.1
	1	2	6	Bal.	4.6	31.5
	1	3	1	Bal.	4.1	35.9
	1	3	2	Bal.	4.3	34.2
	1	3	3	Bal.	4.5	32.6
	1	3	4	Bal.	4.7	30.9
	1	4	0	Bal.	4.3	33.7
	1	4	1	Bal.	4.5	32.0
	1	4	2	Bal.	4.7	30.3
	2	0	6	Bal.	4.1	36.1
	2	0	7	Bal.	4.2	34.4
	2	0	8	Bal.	4.4	32.8
	2	0	9	Bal.	4.6	31.2
	2	1	4	Bal.	4.1	35.5
	2	1	5	Bal.	4.3	33.9
	2	1	6	Bal.	4.5	32.2
	2	1	7	Bal.	4.7	30.6
	2	2	2	Bal.	4.2	35.0
	2	2	3	Bal.	4.4	33.3
	2	2	4	Bal.	4.6	31.7
	2	2	5	Bal.	4.8	30.0
	2	3	0	Bal.	4.2	34.4
	2	3	1	Bal.	4.4	32.8
	2	3	2	Bal.	4.6	31.1
	2	4	0	Bal.	4.7	30.5
	3	0	4	Bal.	4.0	36.2
	3	0	5	Bal.	4.2	34.6
	3	0	6	Bal.	4.4	33.0
	3	0	7	Bal.	4.6	31.4
	3	1	2	Bal.	4.1	35.7
	3	1	3	Bal.	4.3	34.1
	3	1	4	Bal.	4.5	32.4
	3	1	5	Bal.	4.7	30.8
	3	2	0	Bal.	4.2	35.2
	3	2	1	Bal.	4.4	33.5
	3	2	2	Bal.	4.6	31.9
	3	2	3	Bal.	4.7	30.2

4

	Chemical Composition(wt%)				Tensile Strength (kgf/mm^2)	elongation (%)
	A g	B i	I n	S n		
E x a m p l e	3	3	0	Bal.	4.6	31.3
	4	0	2	Bal.	4.0	36.4
	4	0	3	Bal.	4.2	34.8
	4	0	4	Bal.	4.4	33.2
	4	0	5	Bal.	4.6	31.5
	4	1	0	Bal.	4.1	35.9
	4	1	1	Bal.	4.3	34.2
	4	1	2	Bal.	4.5	32.6
	4	1	3	Bal.	4.7	31.0
	4	2	0	Bal.	4.5	32.1
	4	2	1	Bal.	4.7	30.4
C o m p a r a t i v e E x a m p l e	1	0	7	Bal.	3.9	37.5
	1	0	12	Bal.	4.9	29.4
	1	1	5	Bal.	3.9	37.0
	1	1	10	Bal.	4.9	28.8
	1	2	2	Bal.	3.8	38.1
	1	2	7	Bal.	4.8	29.8
	1	3	0	Bal.	3.9	37.5
	1	3	5	Bal.	4.9	29.3
	1	4	3	Bal.	4.9	28.7
	2	0	5	Bal.	3.9	37.7
	2	0	10	Bal.	4.8	29.5
	2	1	3	Bal.	3.9	37.1
	2	1	8	Bal.	4.9	29.0
	2	2	1	Bal.	3.9	36.6
	2	2	6	Bal.	5.0	28.4
	2	3	3	Bal.	4.8	29.5
	2	4	1	Bal.	4.9	28.9
	3	0	3	Bal.	3.8	37.9
	3	0	8	Bal.	4.8	29.7
	3	1	1	Bal.	3.9	37.3
	3	1	6	Bal.	4.9	29.2
	3	2	4	Bal.	4.9	28.6
	3	3	1	Bal.	4.8	29.6
	4	0	1	Bal.	3.8	38.1
	4	0	6	Bal.	4.8	29.9
	4	1	4	Bal.	4.9	29.3
	4	2	2	Bal.	4.9	28.8
P b - 6 3 S n					3.8	30.0
S n - 3 . 5 A g					2.0	70.0

It is known from Table 1 that the solder of the present invention has a tensile strength equal to or greater than 4.0 kgf/mm2 and an elongation equal to or greater than 30% which are satisfactory mechanical properties to attain the object of the present invention.

Thus, by the present invention as described above, a solder with mechanical properties as good as those of conventional Pb-Sn solder is provided.
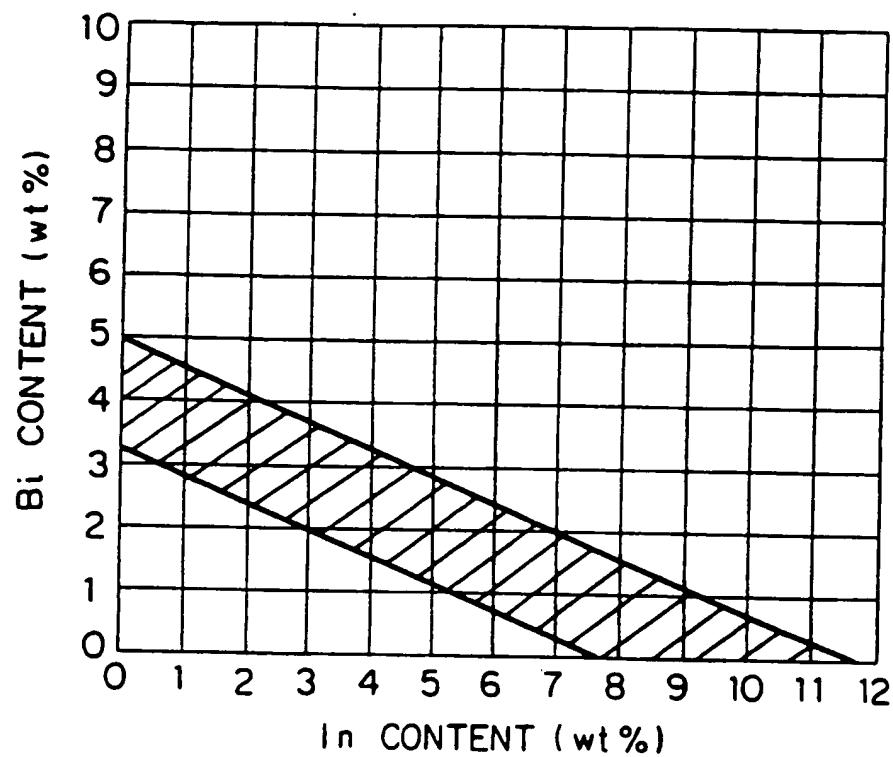
Claims

1. A lead-free solder consisting of 1 to 4 wt% of Ag, either one or both of Bi and In of their respective amounts meeting the conditions that the value of expression (1), A, is equal to or greater than 5.00 and that the value of expression (2), B, is equal to or less than 6.90, and Sn for the balance:

$$A = [Ag\ wt\%] + 1.23\ [Bi\ wt\%] + 0.52\ [In\ wt\%] \tag{1}$$

$$B = [Ag\ wt\%] + 1.19\ [Bi\ wt\%] + 0.50\ [In\ wt\%] \tag{2}$$

2. The lead-free solder of claim 1 which is Sn-Ag-In ternary alloy with the In content smaller than 4 wt%.

FIG. 1

In CONTENT (wt%)

Ag : 1 wt% (Sn: BALANCE)

FIG. 2

In CONTENT (wt/)

Ag: 2wt% (Sn: BALANCE)

FIG. 3

In CONTENT (wt%)

Ag: 3wt% (Sn: BALANCE)

FIG. 4

In CONTENT (wt /)

Ag: 4wt % (Sn: BALANCE)

8
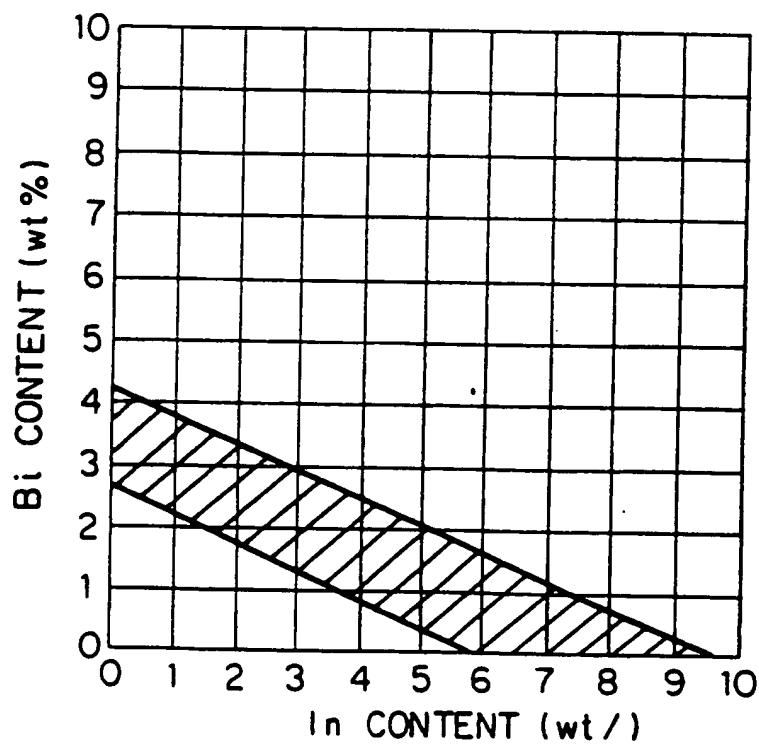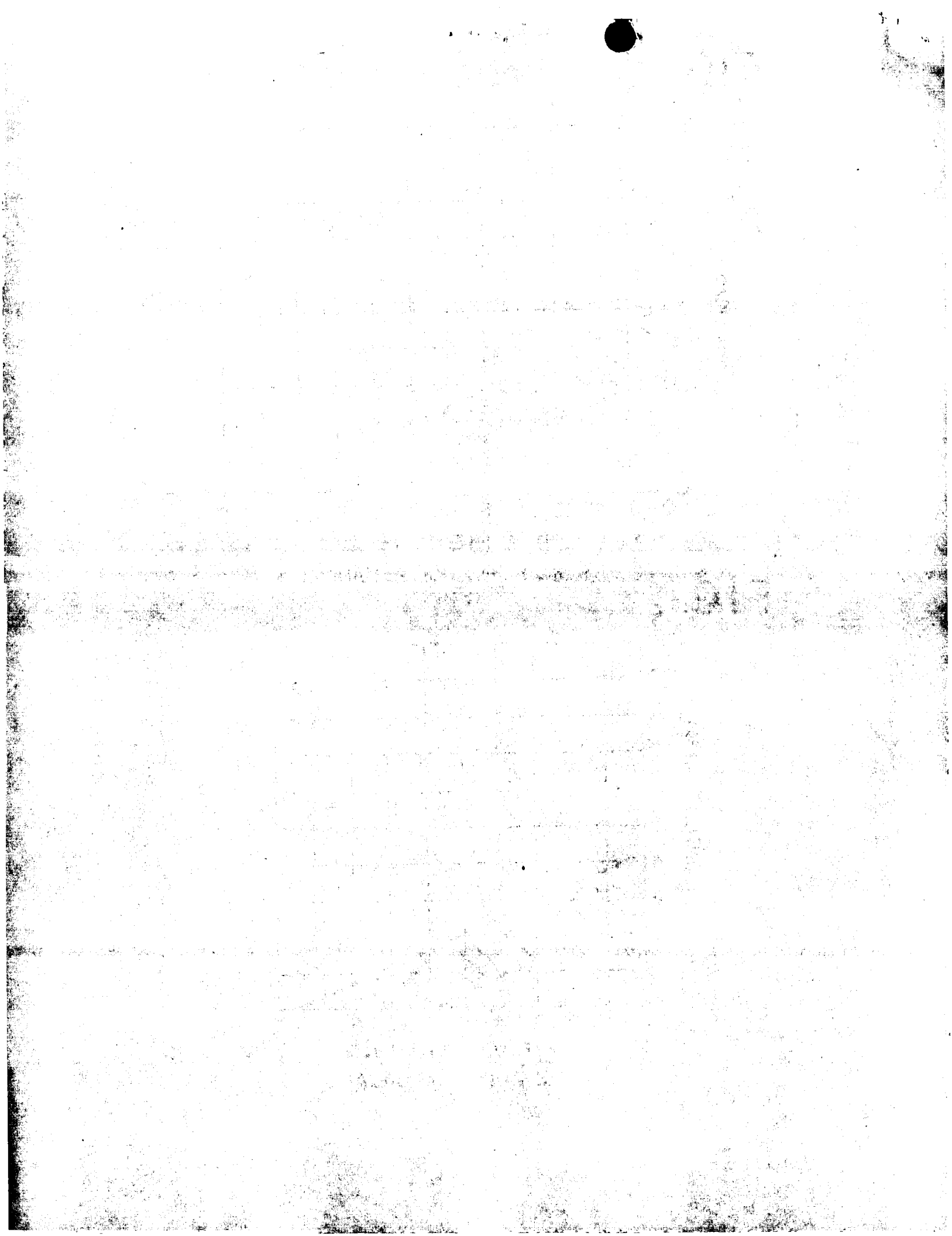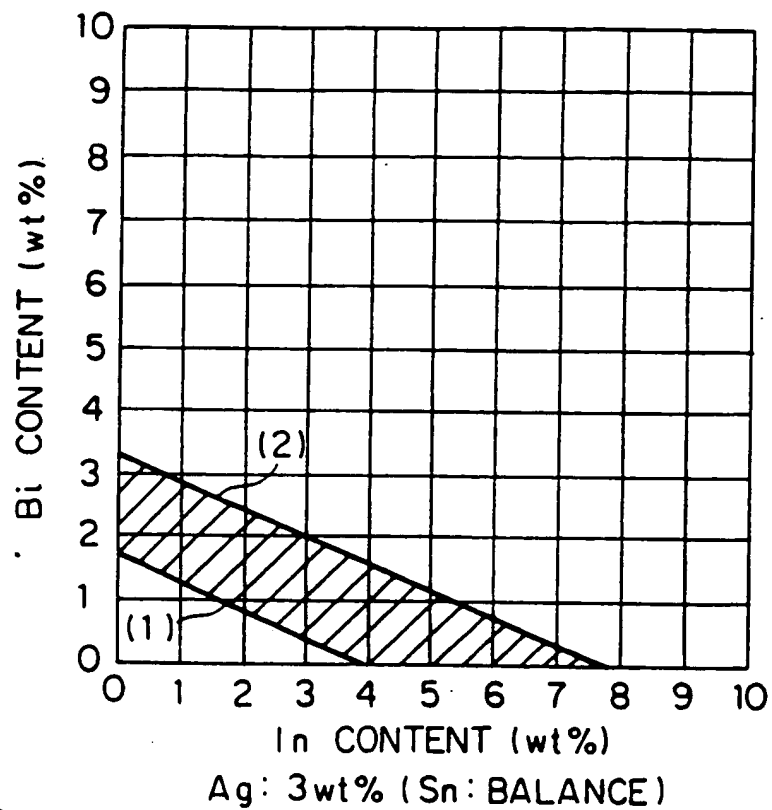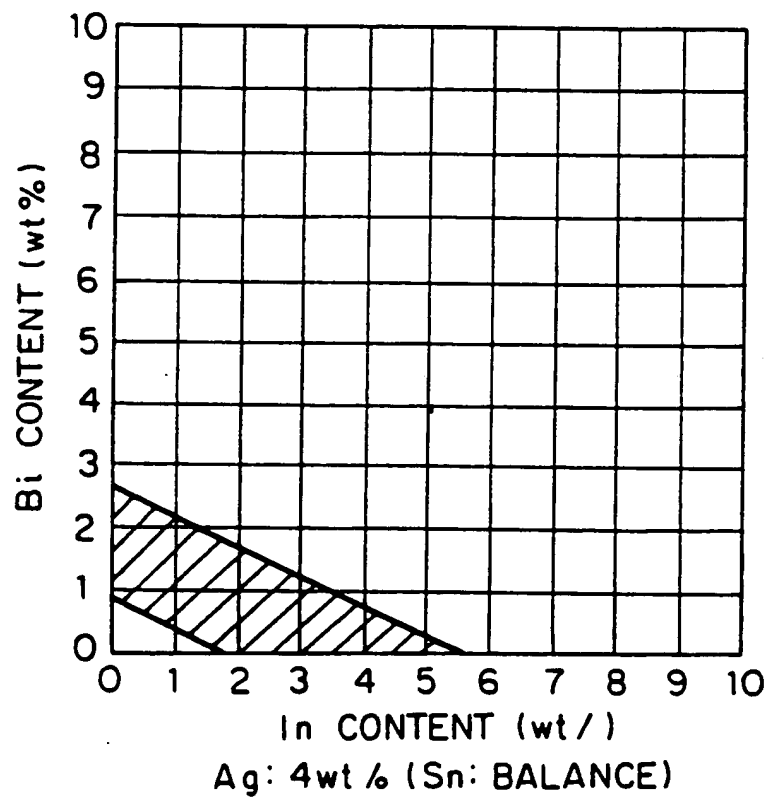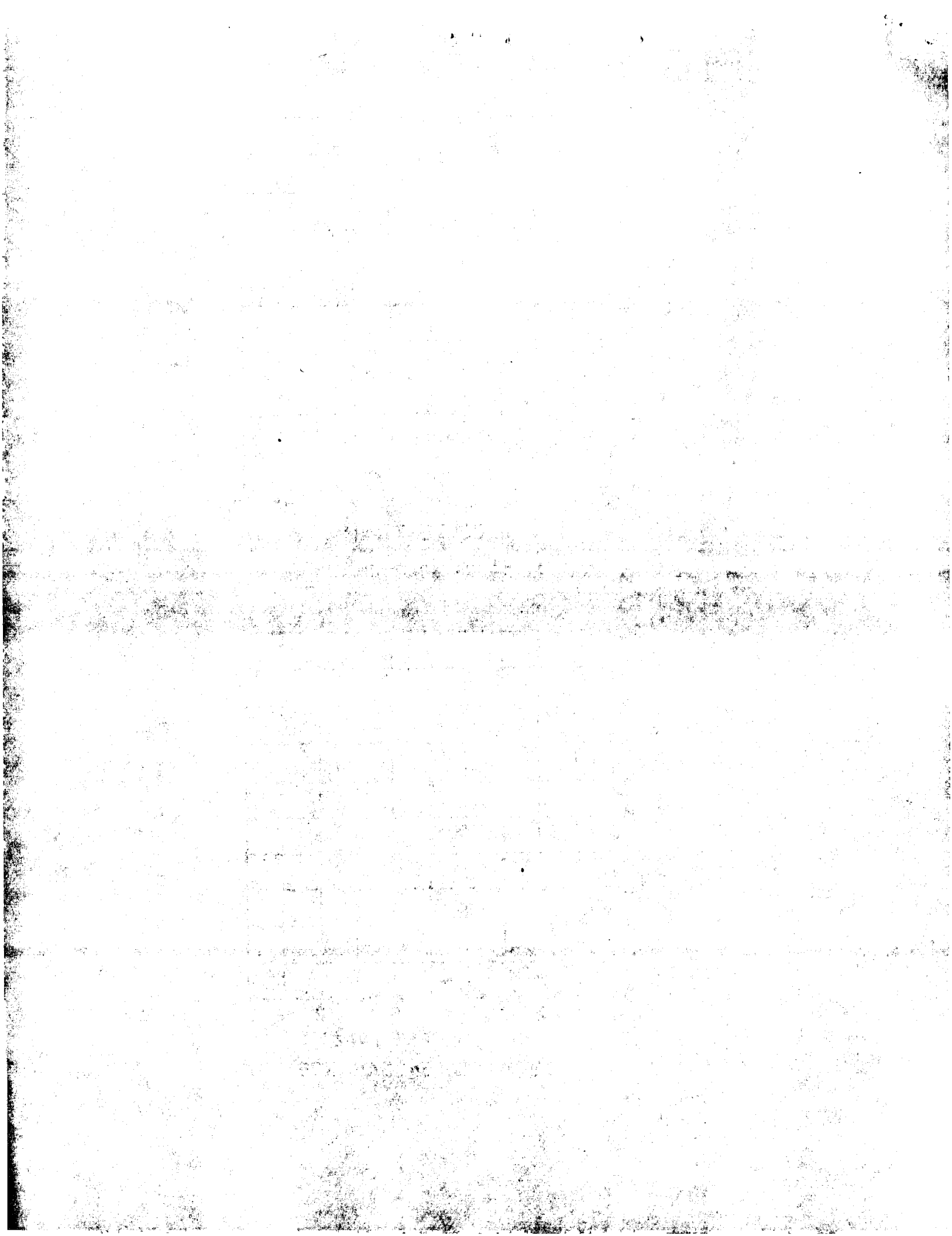
DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 568 952 (THE INDIUM CORPORATION) * claims 1,8; example 1 * ---	1	B23K35/26 //C22C13/00
X	EP-A-0 499 452 (LANCASHIRE FITTINGS) * claims 1,2; table 1 * ---	1	
X	GB-A-131 299 (S.A. DES LAMINOIRS ET CABLERIE) * page 2, line 6 - line 12 * ---	1	
X	PATENT ABSTRACTS OF JAPAN vol. 17 no. 675 (M-1526) ,13 December 1993 & JP-A-05 228685 (MATSUSHITA ELECTRIC) 7 September 1993, * abstract * ---	1	
A	US-A-5 328 660 (S.G. GONYA ET AL) ---		
P,X	EP-A-0 629 466 (INTERNATIONAL BUSINESS MACHINES) * claims 1,2; example 1 * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B23K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 December 1995	Mollet, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document